

CONDUCTIVE LIQUID CRYSTAL DEVICE  
AND ORGANIC ELECTROLUMINESCENCE DEVICE

FIELD OF THE INVENTION AND RELATED ART

5           The present invention relates to an  
electroconductive liquid crystal device, particularly  
a conductive liquid crystal device useful as an  
organic electroluminescence device (hereinafter, the  
term "electroluminescence" being sometimes abbreviated  
10 as "EL" according to common usage in the field).

As for the organic EL device, carrier  
injection-type EL devices utilizing organic solids,  
such as anthracene single crystal, were studied in  
detail in years of 1960's. These devices were of a  
15 single layer-type, but thereafter Tang, et al proposed  
a lamination-type organic EL device comprising a  
luminescence layer and a hole transporting layer  
between a hole injecting electrode and an electron  
injecting electrode. The luminescence mechanism in  
20 these injection-type EL devices commonly includes  
stages of (1) electron injection from a cathode and  
hole injection from an anode, (2) movement of  
electrons and holes within a solid, (3) re-combination  
of electrons and holes, and (4) luminescence from the  
25 resultant single term excitons.

A representative example of the lamination-  
type EL device may have a structure including an ITO

film as a cathode formed on a glass substrate, a ca.  
50 nm-thick layer formed thereon of TPD (N,N'-  
diphenyl-N,N'-di(3-methylphenyl)-1,1'-biphenyl-4,4'-  
diamine), a ca. 50 nm-thick layer thereon of Alq3  
5 (tris(8-quinolinolato)-aluminum), and further a vacuum  
deposition layer of Al-Li alloy as a cathode. By  
setting the work function of the ITO used as the anode  
at 4.4 - 5.0 eV, the hole injection to TPD is made  
easier, and the cathode is composed of a metal which  
10 has as small a work function as possible and also is  
stable. Examples of the cathode metal may include Al-  
Li alloy as mentioned above and also Mg-Ag alloy. By  
the above organization, green luminescence may be  
obtained by applying a DC voltage of 5 - 10 volts.

15           An example using a conductive liquid crystal  
as a carrier transporting layer is also known. For  
example, D. Adam et al (Nature, Vol. 371, p. 141-)  
have reported that a long-chain triphenylene compound  
as a discotic liquid crystal material exhibited a  
20 mobility of  $10^{-3} - 10^{-2}$  cm<sup>2</sup>/V.sec in its liquid  
crystal phase (Dh phase) and a mobility of  $10^{-1}$   
cm<sup>2</sup>/V.sec in its mesophase (an intermediate phase,  
not a liquid crystal phase). Also, as for a bar-  
shaped liquid crystal, Junichi Hanna (Ohyou Butsuri  
25 (Applied Physics), Vol. 68, No. 1, p. 26-) has  
reported that a phenylnaphthalene compound exhibited  
a mobility of  $10^{-3}$  cm<sup>2</sup>/V.sec or higher in its smectic

B phase.

As a trial for using such a liquid crystal for electroluminescence, INGAH STAPFF et al. (Liquid Crystals, Vol. 23, No. 4, pp. 613-617) have reported  
5 an organic EL device using a triphenylene-type discotic liquid crystal. Other reports are found in POLYMERS FOR ADVANCES TECHNOLOGIES, Vol. 9, pp. 463-460 (1998), and ADVANCED MATERIALS (1997), Vol. 9, No. 1, p. 48-.

10 Convention organic EL devices have involved several problems attributable to the use of a low-molecular weight compound in a crystal state. A first problem is that the efficiency of injection of  
15 electrons or holes from electrodes of ITO, etc., to the organic layers is low. This is because minute grain boundary in a crystal state of organic molecules functions as a carrier conduction barrier. Accordingly, organic molecules in an amorphous state are generally used though it incurs a low carrier  
20 injection efficiency. This however has provided a major cause why an organic EL device cannot ensure a large current.

An organic material used in an organic EL device has an electronic structure providing a large  
25 energy gap of ca. 3 eV or larger, thermal excitation-type free electrons are not present in a conduction band, a drive current (spatial charge restriction

current) is principally supplied by injected carriers from the electrodes, so that a low carrier injection efficiency from the electrodes has been a serious problem. As the injection efficiency is low, a large voltage has to be applied in order to ensure a drive current, and the device layer thickness has to be lowered. These factors have caused difficulties, such as a short circuit between the electrodes and an increase in capacitive load.

As a second problem, an organic EL device is liable to be affected by invaded moisture to cause deterioration of luminescence performance and drive performance, thus showing poor durability. In an ordinary organic EL device, the organic layers are disposed in lamination and then the cathode is formed thereon by vapor deposition of a metal film. In this instance, a metal species having a small work function suitable for the cathode is susceptible of oxidation and has a low durability. Even in case of forming a protective film thereon by sputtering, the organic layers are liable to be degraded if the forming temperature is high (with an ordinary limit of 100 °C), and the destruction of the device structure due to the film stress is also problematic.

On the other hand, as a problem accompanying the use of a conducive liquid crystal for constituting a carrier transporting layer, it is difficult to align

5  
10

## SUMMARY OF THE INVENTION

15

20

25

According to another aspect of the present invention, there is provided an organic

The present invention further provides an organic electroluminescence device comprising: a  
15 conductive liquid crystal device which includes a pair of oppositely disposed electrodes and at least two organic layers disposed between the electrodes, wherein said at least two organic layers include at least one liquid crystalline organic layer having  
20 plural regions of different electroconductivities resulting in different luminances of luminescence from the device.

These and other objects, features and advantages of the present invention will become more apparent upon a consideration of the following description of the preferred embodiments of the present invention taken in conjunction with the

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 2A is a schematic sectional view of an organic EL device according to Example 1 of the invention, and Figure 2B is a corresponding bottom plan view.

## 15 DESCRIPTION OF THE PREFERRED EMBODIMENTS

25           A high electric field on the order of 10  
volts/100 nm has been required for the drive of an  
organic EL device because of (1) a low mobility of

carriers (holes and electrons) through organic layers and (2) a low efficiency of injection of carriers into the organic layers from the electrodes. Organic materials used in organic EL devices have a broad band gap of ca. 3.0 eV, so that thermal excitation-type free electrons are not present in a conduction band (LUMO: lowest unoccupied molecular orbital), and drive current is principally supplied by a tunnel current injected from the electrodes. The injection efficiency of the current is known to be remarkably affected not only by the work functions of the electrodes and a level gap between LUMO and HOMO (Highest Occupied Molecular Orbital) of the organic materials but also by the molecular alignment and structure of the organic materials. However, in order to attain a sufficient drive current by using ordinary organic compounds (such as TPD,  $\alpha$ -NPD (bis[N-(1-naphthyl)-N-phenyl]benzidine), TAZ-01 (3-(4-biphenyl)-4-phenyl-5-(4-tert-butylphenyl)-1,2,4-triazole), Alq3, etc.) in ordinary EL devices, it has been necessary to apply a high electric field (on the order of 10 V/100 nm) across the organic layer-electrode boundaries. Further, as the mobility of the organic materials is on the order of  $10^{-6}$  -  $10^{-3}$  cm<sup>2</sup>/V.sec, it is also necessary to apply a high electric field in order to ensure a drive current. Some improvement to the above problem has been given by using a conductive liquid



crystal for constituting a liquid crystalline charge injection layer as proposed by our research group (EP-A 1083613 and EP-A 1089596).

5 The use of a conductive liquid crystal for constituting a charge injection layer is effective because of the following reasons and functions.

(1) Some conductive liquid crystallines have a mobility exceeding  $10^{-2}$  cm<sup>2</sup>/V.sec (D. Adam, et al; Nature Vol. 371, p. 141-).

10 (2) A conductive liquid crystal causes a phase transition at a higher temperature to assume a lower order liquid crystal phase, such as nematic phase or discotic disordered phase, thereby showing a good alignment characteristic to cause alignment of liquid  
15 crystal molecules over an electrode surface.

(3) Especially, a discotic liquid crystal generally has a structure including a core of, e.g., triphenylene, and side chains attached to the periphery of the core for developing mesomorphism  
20 (liquid crystal property). The side chains generally exhibit poor wettability with a substrate of a metal or a metal oxide (such as ITO), so that in the liquid crystal state of the discotic liquid crystal, the core is aligned parallel to the electrode surface, whereby  
25 the  $\pi$ -electron resonance plane of the core is aligned parallel to the electrode surface, thereby facilitating carrier transfer with the electrode.

Accordingly, it is possible to provide a higher injection efficiency than an ordinary organic compound in an amorphous state.

5 This effect can also be expected for an ordinary bar-shaped liquid crystal having a molecular structure including a phenyl group or a naphthalene group having a  $\pi$ -electron resonance plane.

10 (4) The formation of a conductive liquid crystal layer as a carrier transporting layer by vacuum deposition is particularly effective. A liquid crystal film layer formed by vacuum deposition has a coarse molecular packing state, the re-alignment thereof by heating is very easy. This is particularly true with a liquid crystal film formed by vacuum  
15 deposition on a substrate at a temperature close to or below  $T_g$  (glass transition temperature) of the liquid crystal giving a stably coarse film structure.

20 (5) A high-order liquid crystal phase having a higher degree of order has a low fluidity; and the alignment thereof in the high-order liquid crystal phase per se is difficult, whereas the alignment characteristic thereof can be improved if the liquid crystal layer is sandwiched between films having a power of aligning  $\pi$ -electron conjugated planes  
25 parallel thereto. Realignment by heating up to the isotropic phase is not desirable for device formation sometimes because of a strong dissolving power of the

liquid crystal material in a liquid phase to other organic materials, but the dissolution problem is not encountered at a boundary with a metal film. In the case of sandwiching a liquid crystal with metal films, one of them is required to allow light-transmission. For example, in the case of using a gold film, the film may be formed as an island-like uneven film, but the alignment thereby of a liquid crystal can be improved than in the absence of such a gold film.

(6) A molecule exhibiting mesomorphism can re-organize molecular disposition at the electrode surface by re-aligning post treatment. This can facilitate the injection efficiency. The post treatment can exhibit a large effect even when it is performed by heating only to a liquid crystal phase temperature if it provides a lower viscosity. The heating to the isotropic temperature, while it is effective for the re-alignment, has to be suppressed to a temperature below the  $T_g$  of other organic materials used together therewith.

(7) At a boundary of a luminescence layer with a liquid crystal layer or an intermediate metal layer, it is effective to insert a protective layer comprising a material having a function of transporting a carrier of the same type.

In the present invention, such a conductive liquid crystal layer is formed while noting the above



(cathode) 6 disposed in this order on the substrate 1, wherein the liquid crystalline organic layer 3 is provided with plural regions having mutually different electroconductivities including non-aligned liquid crystal regions 3a having a lower conductivity and aligned liquid crystal regions 3b having a higher conductivity.

The liquid crystalline organic layer 3 comprises a liquid crystalline or mesomorphic compound having a liquid crystal phase at some temperature, inclusive of low-molecular weight (non-polymeric) conductive liquid crystals and polymeric conductive liquid crystals. The conductive liquid crystal may suitably have a  $\pi$ -electron resonance structure, which is generally given by an aromatic ring. Examples thereof may include: triphenylene ring, naphthalene ring and benzene ring, as representative, and also pyridine ring, pyrimidine ring, pyridazine ring, pyrazine ring, tropone ring, azulene ring, benzofuran ring, indole ring, indazole ring, benzothiazole ring, benzoxazole ring, benzimidazole ring, quinoline ring, isoquinoline ring, quinazoline ring, quinoxaline ring, phenanthrene ring and anthracene ring.

The conductive liquid crystal used in the present invention may preferably comprise a discotic liquid crystal or a smectic liquid crystal. A discotic liquid crystal may generally have a core

structure which may be given by an aromatic ring as mentioned above for the  $\pi$ -electron resonance structure, as represented by triphenylene ring (or skeleton). Further examples thereof may include

5 truxene skeleton, metal-phthalocyanine skeleton, phthalocyanine skeleton, dibenzopyrene skeleton, metal-naphthalocyanine skeleton, dibenzopyrene skeleton, and hexabenzocoronene skeleton.

As for the electrode materials used in the

10 present invention, examples of material constituting the anode 2 may include: indium oxide, tin oxide,  $\text{Cd}_2\text{SnO}_4$ , zinc oxide, copper iodide, gold and platinum, in addition to ITO used in Examples described hereinafter. Examples of material constituting the

15 cathode 6 may include: alkali metals, alkaline earth metals and alloys of these, inclusive of sodium, potassium, magnesium, lithium, sodium-potassium alloy, magnesium-indium alloy, magnesium-silver alloy, aluminum, aluminum-lithium alloy, aluminum-copper

20 alloy, aluminum-copper-silicon alloy.

Further, examples of materials for the luminescence layer 5 may include: in addition to Alq3, BeBq (bis(benzoquinolinolato)beryllium), DTVB2 (4,4'-bis(2,2-di-p-tolylvinyl)biphenyl),  $\text{Eu}(\text{DBM})_3(\text{Phen})$

25 (tris(1,3-diphenyl-1,3-propanediono)-monophenanthroline) $\text{Eu}(\text{III})$ ), and further, diphenyl-ethylene derivatives, triphenylamine derivatives,

diaminocarbazole derivatives, bisstyryl derivatives,  
benzothiazole derivatives, benzoxazole derivatives,  
aromatic diamine derivatives, quinacridone compounds,  
perylene compounds, oxadiazole derivatives, coumarin  
5 compounds, anthraquinone derivatives, distyrylarylene  
derivatives (DPVBi), and oligothiophene derivatives  
(BMA-3T).

Further, as mentioned above, a protective  
layer can be inserted adjacent to the liquid  
10 crystalline organic layer 3. The protective layer may  
preferably comprise a material having a large volume  
so as to exhibit little diffusivity into liquid  
crystalline materials used in the liquid crystalline  
organic layer 3. It is further preferred that the  
15 protective layer material does not have a liquid  
crystal phase of an order equivalent to or lower than  
that of a disordered phase at an operation  
temperature, and more preferably is a non-liquid  
crystal material. Examples thereof may include:

20  $\alpha$ -NPD: bis[N-1-(naphthyl)-N-phenyl]benzidine,  
1-TANTA: 4,4',4''-tris(1-naphthylphenylamino)-  
triphenylamine,  
2-TANTA: 4,4',4''-tris(2-naphthylphenylamino)-  
triphenylamine,  
25 TCTA: 4,4',4''-tris(N-carbazoyl)triphenylamine,  
p-DPA-TDAB: 1,3,5-tris[N-(4-diphenylaminophenyl)-  
phenylamino]benzene,

TOP SECRET

**DTATA:** 4,4',4''-tris(diphenylamino)triphenylamine,

### [ Examples ]

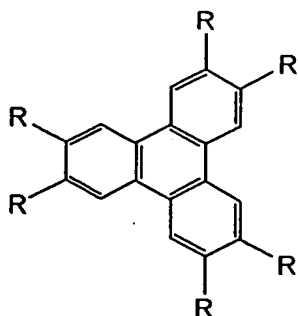
(Example 1)

More specifically, on a glass substrate 11 held at 200 °C, a 70 nm-thick ITO film was formed as a hole-injecting anode 12 by sputtering using a target of In 90 wt. % and Sn 10 wt. % while flowing Ar gas at 200 sccm and O<sub>2</sub> gas at 3 sccm. The ITO film showed a work function of ca. 4.35 eV after the sputtering but was then exposed to ultraviolet rays from a low-pressure mercury lamp to have an elevated work function of ca. 4.6 eV.

The above-treated glass substrate 11 having an ITO film 12 was placed in a vacuum chamber held at a pressure below  $2.67 \times 10^{-3}$  Pa ( $2 \times 10^{-5}$  torr), and a ca. 35 nm-thick layer of HHOT (hexabis(hexyloxy)-triphenylene) of a formula shown below was formed as a



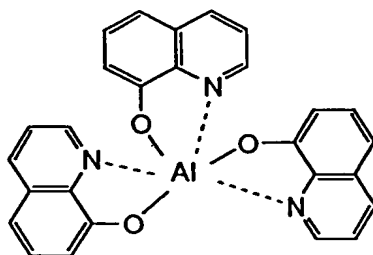
conductive liquid crystal layer 13 on the ITO film 12  
by vacuum deposition at a rate of ca. 0.1 nm/sec at a  
pressure of  $1.33 \times 10^{-3}$  Pa ( $1 \times 10^{-5}$  torr) according to  
the resistance heating vacuum deposition method. HHOT  
exhibited a mobility of  $1 \times 10^{-3}$  cm<sup>2</sup>/V.sec at ca. 70 °C  
or below according to the time-of-flight method.  
Incidentally, HHOT is a discotic liquid crystal  
causing a transition from crystal to discotic  
disordered phase at 65 °C and a transition to  
isotropic phase at 98 °C.



HHOT

R = C<sub>6</sub>H<sub>13</sub>O

Then, on the HHOT layer 13, a luminescence layer 15 of Alq<sub>3</sub> represented by a structural formula shown below was formed in a thickness of 60 nm by vacuum deposition at a rate of ca. 0.1 nm/sec under a pressure of  $1.33 \times 10^{-3}$  Pa ( $1 \times 10^{-5}$  torr).



Then, the Alq<sub>3</sub> layer 15 was further coated with a cathode metal 16 comprising a 50 nm-thick layer of Al-Li alloy (Li content = 1.8 wt. %) and a 150 nm thick Al layer, respectively formed by vacuum deposition, to form a device structure roughly as shown in Figure 2A.

In this state, all the organic layers 13 and 15 were in an amorphous (non-aligned) state. In this state, the liquid crystal layer 13 was locally irradiated with GaAlAs laser beam (beam diameter = ca. 20  $\mu$ m, 10 mW) and cooled by standing to be provided with locally aligned portions 13b showing a higher conductivity than non-irradiated, non-aligned regions 13a.

As a result, an organic EL device having a sectional structure as shown in Figure 2A was

obtained.

The organic EL device was subjected to voltage application under an electric field of 12 volts/100 nm. As a result, the device exhibited luminescence with different luminescences at laser-irradiated parts 13b and non-irradiated parts 13a as shown in Table 1 below and exhibited a display state as shown in Figure 2B giving a sufficient contrast between the irradiated luminescent parts 17 and non-irradiated non-luminescent parts 18.

Table 1

	Current (mA/cm <sup>2</sup> )	Luminance (cd/m <sup>2</sup> )
Laser-irradiated aligned parts	3.593	120
Non-irradiated non-aligned parts	0.05	1.5

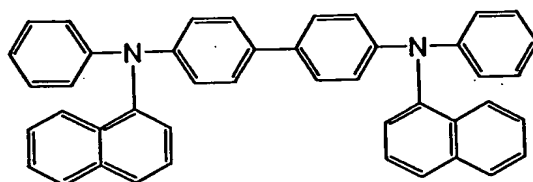
(Example 2)

An organic EL device having a sectional structure as shown in Figure 3 including a pixel structure and a conductive liquid crystal layer 53 having a higher conductivity region 53b corresponding to a selected pixel formed by high voltage application was prepared in the following manner.

A glass substrate 51 coated with a 70 nm-thick ITO layer (anode) 52 and a ca. 35 nm-thick HHOT layer (conductive liquid crystal layer) 53 was prepared in the same manner as in Example 1.

Then, on the HHOT layer 53, a protective layer 54 of  $\alpha$ NPD represented by a structural formula shown below was formed in a thickness of 60 nm by vacuum deposition at a rate of ca. 0.1 nm/sec under a pressure of  $1.33 \times 10^{-3}$  Pa.

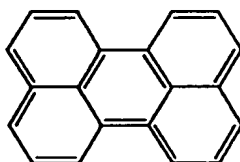
$\alpha$ -NPD



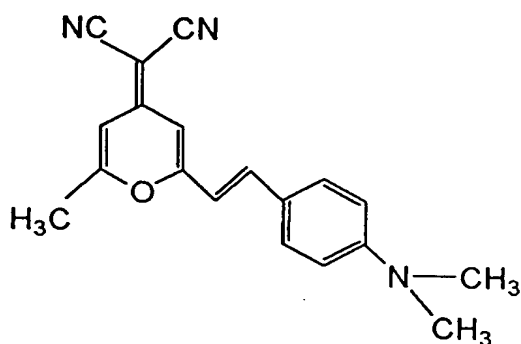
Luminescence organic layer segments 55a - 55c exhibiting different luminescent wavelengths were respectively formed in a thickness of 50 nm on the protective layer 54 by vacuum deposition through a mask under the conditions of a pressure of  $1 \times 10^{-5}$  torr and a deposition rate of ca. 0.1 nm/sec. The organic layers 55a - 55c were respectively formed of Alq3 alone, Alq3 doped with 5 wt. % of perylene for shifting the luminescence wavelength to a shorter wavelength side, and Alq3 doped with 5 wt. % of DCM (a styryl dye) for shifting to a longer wavelength side. The structural formulae for the above-mentioned

perylene and DCM are shown below.

perylene



DCM



The above-prepared organic layers 55a - 55c were respectively coated with cathode metals 56 each comprising a 50 nm-thick layer of Al-Li alloy (Li content = 1.8 wt. %) and a 150 nm-thick Al layer, respectively formed by vacuum deposition, to obtain an organic EL device having a structure as shown in Figure 3.

The above-prepared device was confirmed to exhibit luminescence of respective colors at segments 55a - 55c at an increased luminance at an increased current when maintained at 75 °C.

In this example, only a selected pixel

portion of the organic layers including a luminescence segment (55a in Figure 3) was supplied with a high electric field of 15 volts/100 nm for 3 min. at 30 °C, and the other segments (55b and 55c in Figure 3) were not subjected to the high voltage application treatment. Thereafter, all the segments 55a - 55c were supplied with a drive electric field of 5 volts/100 nm at 30 °C. As a result, the segment 55c subjected to the high-voltage application treatment exhibited a selectively high luminance as shown in Table 2 below.

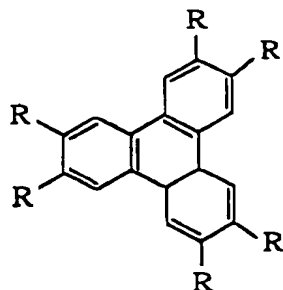
Table 2

	Current (mA/cm <sup>2</sup> )	Luminance (cd/m <sup>2</sup> )
High voltage treatment applied (55a, 53b)	12	300
High voltage treatment not applied (55b-55c, 53a)	<0.05	0

(Example 3)

An organic EL device having a sectional structure as shown in Figure 3 (before formation of a different conductivity region 53b) was prepared in the

same manner as in Example 2 except for using HPOT (hexabis(pentyloxy)triphenylene) of a formula shown below was used instead of HHOT for providing a conductive liquid crystal layer 53.



HPOT  $R = C_4H_9O$

After the above device preparation, a portion of the conductive liquid crystal layer 53 (corresponding to a luminescence segment 55a in Figure 3) was irradiated with GaAlAs laser beam (beam diameter = ca. 20  $\mu m$ , 10 mW) similarly as in Example 1 to form a different conductivity region (53b shown in Figure 3).

Thereafter, the device was subjected to application of an electric field of 12 volts/100 nm, whereby the irradiated part and non-irradiated parts exhibited different luminances as shown in Table 3 below.

5

10

15

20

25

As described above, according to the present invention, it has become possible to provide an



10

15

20

25